Journal of Power Sources 247 (2014) 883–889

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Composite anodes based on nanotube titanium oxide from electro-oxidation of Ti metal substrate☆

A. Pozio [a, *], M. Carewska [a], F. Mura [b], R. D'Amato [c], M. Falconieri [d], M. De Francesco [a], G.B. Appetecchi [a, *]

[a] UTRINN-IFC, ENEA (Agency for New Technologies, Energy and Sustainable Economic Development), Via Anguillarese 301, Rome 00123, Italy
[b] Department of Fundamental and Applied Science for Engineering, University of Rome, "La Sapienza", Via Antonio Scarpa 14, 00185 Rome, Italy
[c] UTAPRAD-MNF, ENEA, Via Enrico Fermi 45, 00044 Frascati, Rome, Italy
[d] UTAPRAD, ENEA, Via Anguillarese 301, 00123 Rome, Italy

HIGHLIGHTS

- Nanotube TiO_2 as anode material for lithium batteries was electrosynthesized from Ti metal.
- Good performance shown by electronic conductor-free nanotube TiO_2 anodes.
- Superior performance with respect to commercial TiO_2 and TiO_2 from laser pyrolysis.

ARTICLE INFO

Article history:
Received 29 April 2013
Received in revised form
20 August 2013
Accepted 2 September 2013
Available online 11 September 2013

Keywords:
Titanium oxide
Nanotubes
Electrosynthesis
Composite anodes
Lithium batteries

ABSTRACT

In this manuscript is reported an investigation on lithium-ion battery composite anodes based on nanotube titanium oxide active material obtained from electrochemical oxidation of titanium metal substrates. Nanotube TiO_2 showed a good nominal capacity, particularly taking into account that no electronic conductive additive as well as no binder was incorporated into the TiO_2 material. The performance of nanotube titanium oxide anode tapes was compared with that of electrodes based on TiO_2 both commercially available and obtained from laser pyrolysis. Cycling tests have indicated that the anodes based on electrosynthesized nanotube TiO_2 exhibit the best performance in terms of capacity values and rate capability in combination with very good capacity retention and coulombic efficiency leveling 100% even at high rates.

1. Introduction

Rechargeable lithium batteries are excellent candidates for the next generation power sources [1,2] because of their high gravimetric and volumetric energy with respect to other cell chemistries. The lithium-ion battery technology is based on the use of electrode materials able to reversibly intercalate Li^+ cations, e.g., a lithium transition metal oxide (LiMO) is used for the positive electrode (cathode) whereas a carbonaceous active material (generally graphite) is used for the negative electrode (anode). However, the performance of graphite anodes strongly depends on the stability of the passive layer (SEI), formed by the products resulting from the electrochemical reaction with the electrolyte during the first charge of the battery, at electrolyte/anode interface [1,2]. In addition, lithiated graphite electrode is strongly reducing, as it operates close to the potential of Li metal. The interface between lithiated graphite and the electrolyte is stable only because of the presence of SEI [3,4]. Therefore, eventual breaking (due to overheating and/or overcharging of the battery) of SEI is not welcome since it leads to electrochemical device failure with consequent fire and/or explosion [3,4].

Alternative anode materials are currently under worldwide investigation for replacing the graphite electrode. Among these, titanium oxide (TiO_2) results much safer than graphite as anode

* Corresponding authors.
E-mail addresses: alfonso.pozio@enea.it (A. Pozio), gianni.appetecchi@enea.it (G.B. Appetecchi).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.09.003

material since no growth passive layer occurs (or is stringently required) at interface with the electrolyte [5]. The adoption of titanium oxide is due to its *zero* strain structure during the intercalation process, this leading to an exceptional cycling stability [5]. In addition, TiO_2 exhibits several advantages as large capacity, high cycling stability (e.g., the material is able to operate within the electrochemical stability window of the electrolyte), very flat charge and discharge plateaus, coulombic efficiency close to 100%, low cost and environmental impact. Titanium oxide was initially investigated in the 80's by Ohzuku et al. [6] and Zachau-Christiansen et al. [7] and, successively, by Kavan et al. [8] who have recorded a nominal capacity equal to 168 mA h g^{-1} in microsize TiO_2. Higher capacity values in combination with good rate performance were exhibited from nanoscale TiO_2, due to additional lithiation shown from $LiTiO_2$, as reported by Gao et al. [9], Li et al. [10], Xu et al. [11], Bao et al. [12] and Bresser et al. [13]. Capacity values exceeding 200 mA h g^{-1} were also obtained in commercial nanocrystalline titanium oxide material, even if at low current rates, by Moretti et al. [14].

However, TiO_2 shows poor electronic conduction, thus needing to be careful coated with an appropriate electron conductor (carbon) for use in practical devices. At the same time, large efforts are devoted to synthesize titanium oxide materials having nanometric particle size. Among these, nanotube TiO_2 represents an appealing compound, resulting one of the most investigated nanoscale active materials for lithium battery systems [15].

Nanosize TiO_2 can be prepared through different procedures and, among them, electrochemical methods as proposed by Macak et al. [16,17]. A few of us have previously reported a new electrochemical route for obtaining well-aligned, regular TiO_2 nanotubes from a titanium metal substrate [18,19]. In the present manuscript we present the results of a physicochemical and electrochemical investigation performed on composite anodes based on electrosynthesized nanotube titanium oxide as the active material. The electrochemical performance of composite nanotube titanium oxide anode tapes was compared with that of Ti-supported, carbon-free, TiO_2 nanotubes and of electrodes based both on TiO_2 both commercially available and obtained in lab-scale from laser pyrolysis.

2. Experimental

2.1. Electrosynthesis of titanium oxide

Titanium oxide nanotubes were prepared through electrochemical oxidation of titanium metal (provided from Titania) discs having diameter and thickness equal to 15 mm–0.5 mm, respectively. Preliminary results were reported elsewhere [18,19]. The samples, previously encapsulated in a PTFE mount, exhibit electrochemical active areas equal to 1 cm^2. The growth of TiO_2 nanotubes onto the Ti° substrate surface was allowed through a five consecutive step procedure route:

a) *Chemical etching of Ti° surface*: the titanium disc samples were undergone to chemical etching in a HF (provided from Carlo Erba), 5 vol.%, and HNO_3 (Air Products), 15 vol.%, water solution. Such a treatment allows removing the passive layer and impurities onto the titanium surface.
b) *Preliminary galvanostatic oxidation*: this step allows obtaining a uniform and homogeneous TiO_2 layer onto the titanium coin. The Ti° disc, used as the working electrode, was coupled with a Pt° counter electrode in a two-electrode cell containing a 1 M KOH (Carlo Erba) aqueous electrolyte. Successively, a current density equal to 1 mA cm^2 was applied for 3 min (25 °C) by a Solartron 1286 Electrochemical Interface.
c) *Potentiostatic oxidation*: The growth of the TiO_2 nano-tubes was promoted through potentiostatic oxidation of the Ti° electrode (working), coupled with a Pt° counter electrode, in ethylene glycol (Ashland) electrolyte containing de-ionized water (1 wt.%) and NH_4F (Carlo Erba, 0.2 wt.%). A voltage equal to 60 V has been applying for 3 h by a potentiostat/galvanostat Aldrich PS251-2. The current flow through the cell was detected by a potentiometer/galvanometer Keithley 2000 and recorded (as a function of the time) by a Madge-Tech Volt101 equipment in series with a 300 Ω resistance (Leeds and Northrup).
d) *Vacuum drying*: The samples obtained from step (*c*) were vacuum dried at 90 °C for 3 h to remove the residual water from the oxidation steps.
e) *Thermal annealing*: Finally, the vacuum dried samples were thermally annealed at 580 °C (heating rate equal to 2 °C min^{-1}) for 1 h into a Lenton oven in order to crystallize the TiO_2 nanotubes.

The electrosynthesis preparation route described above allowed to obtain self-standing, nanotube TiO_2 anodes (Fig. 1, panel A) having an active material mass loading ranging from 1 mg cm^{-2} to about 3.5 mg cm^{-2}.

2.2. Titanium oxide prepared through laser pyrolysis

Nanoscale (e.g., particle size ranging from 20 to 30 nm) titanium oxide (mainly composed of the crystalline anatase phase as shown by Raman measurements) was synthesized through a laser pyrolysis route, performed using titanium tetra-isopropoxide as the

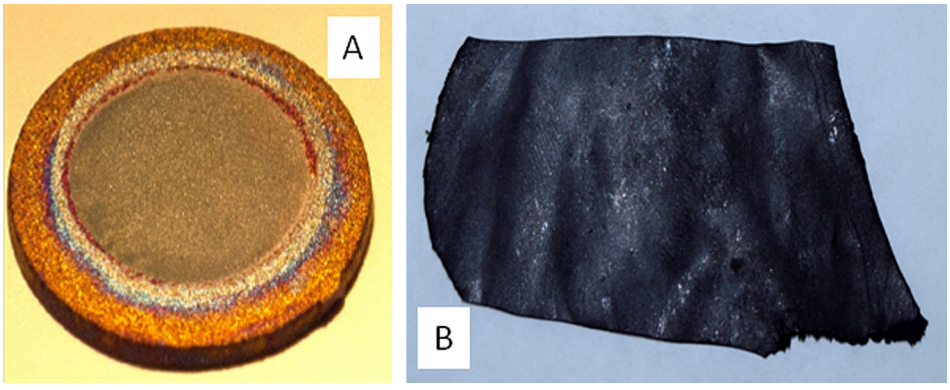

Fig. 1. Picture of a nanotube TiO_2 anode supported onto a Ti° metal substrate (panel A) and a composite anode tape (panel B) based on nanotube TiO_2 as the active material.